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# Neutron Reflectivity Studies of Soft Matter at the Spallation Neutron Source

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*Spallation Neutron Source, ORNL*

September 10, 2003

# Outline

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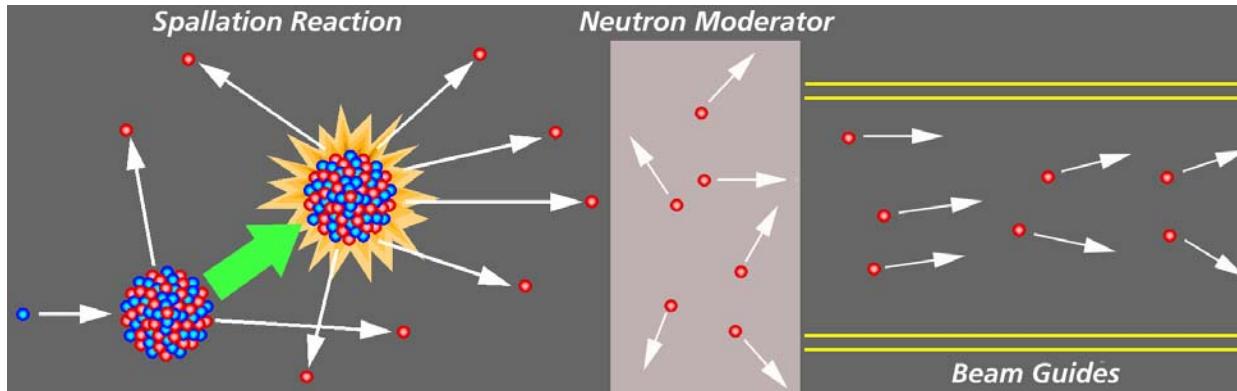


- I. The Spallation Neutron Source
- II. Neutron Reflectivity
- III. What the Future Holds



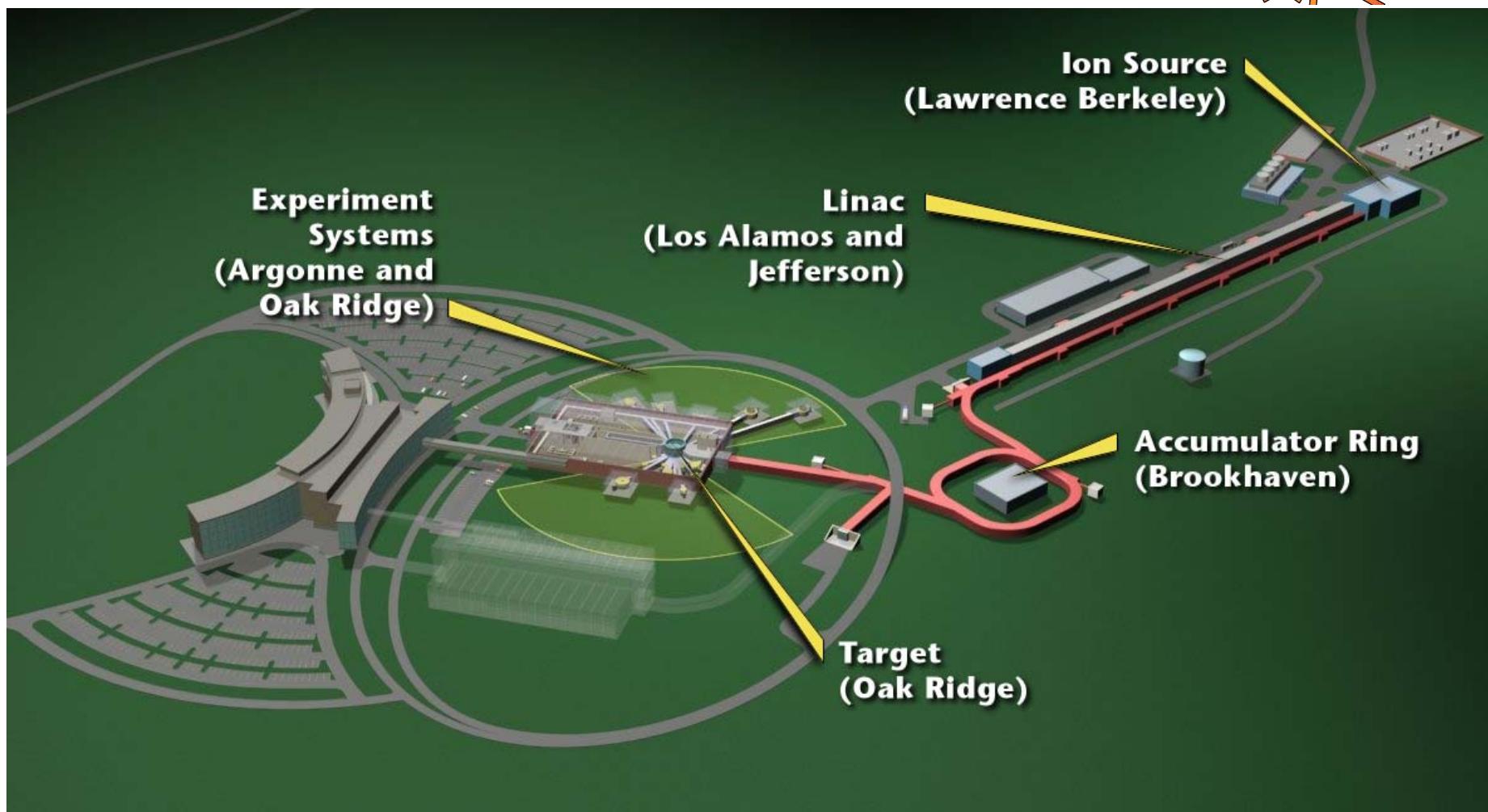
# I. The Spallation Neutron Source

# Spallation



- Protons accelerated and smashed into Hg target
- Neutrons evaporate off of Hg nuclei (spallation)
- Neutrons slowed down by  $H_2$  or  $H_2O$  moderators
- Neutrons piped to instruments

# Hardware - SNS



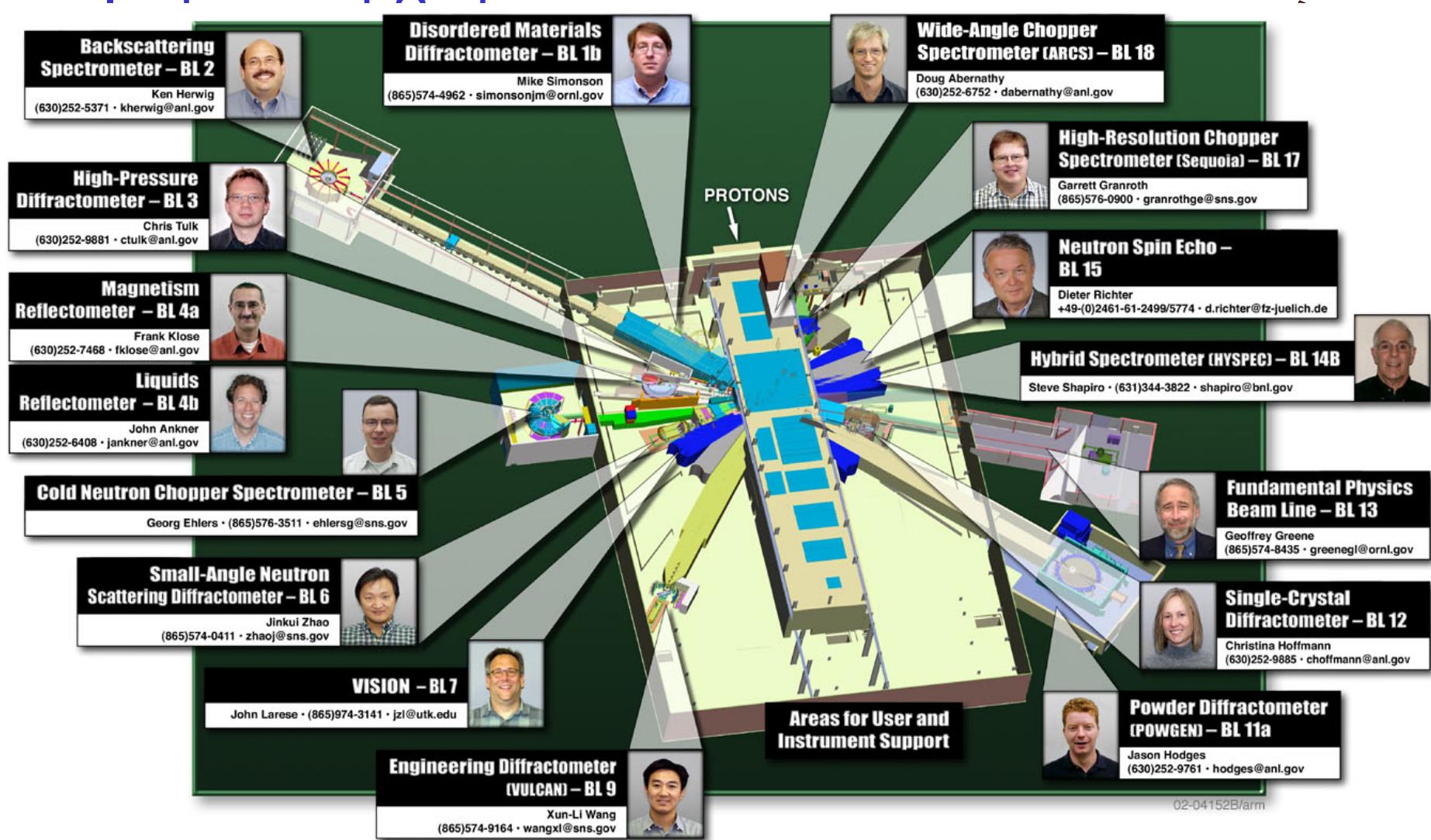
# Target/Instruments Buildings



January 2003



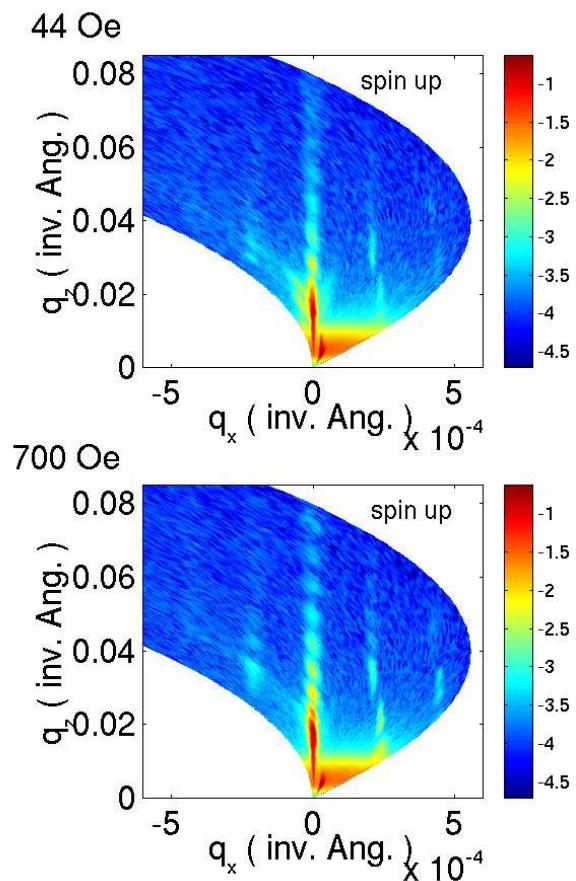
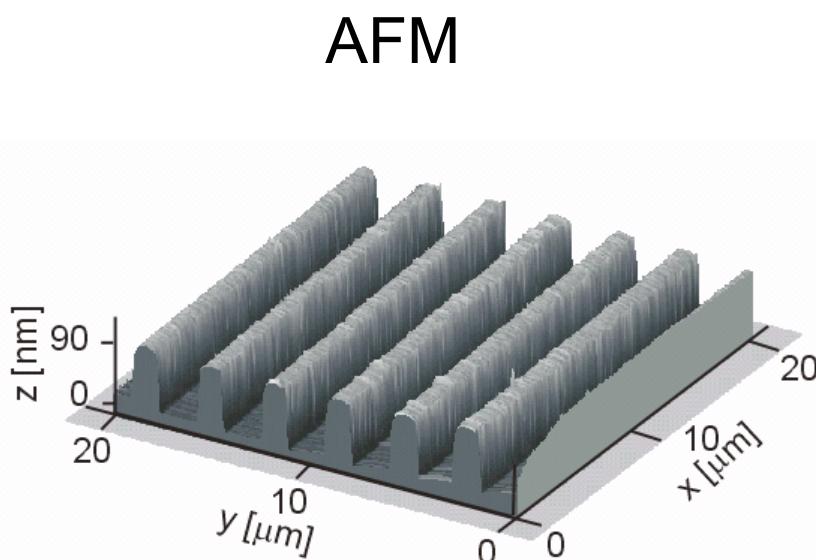
August 2003





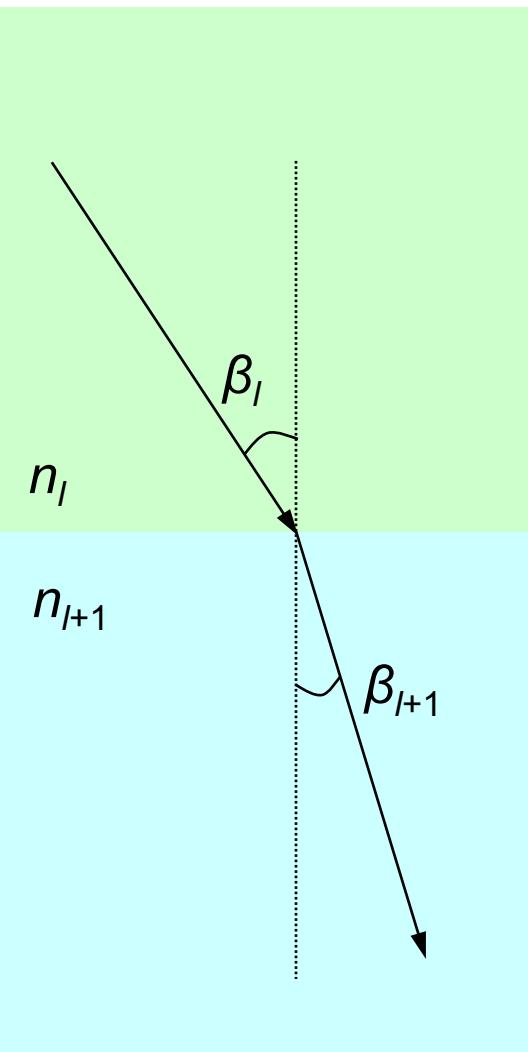
## II. Neutron Reflectivity

# Wave probes image in reciprocal space



[K. Theis-Bröhl, et al., Phys. Rev. B, in press]

# Snell's Law



## Snell's Law

$$n_l \sin \beta_l = n_{l+1} \sin \beta_{l+1}$$

For  $n_{l+1} < n_l$ , can have total reflection

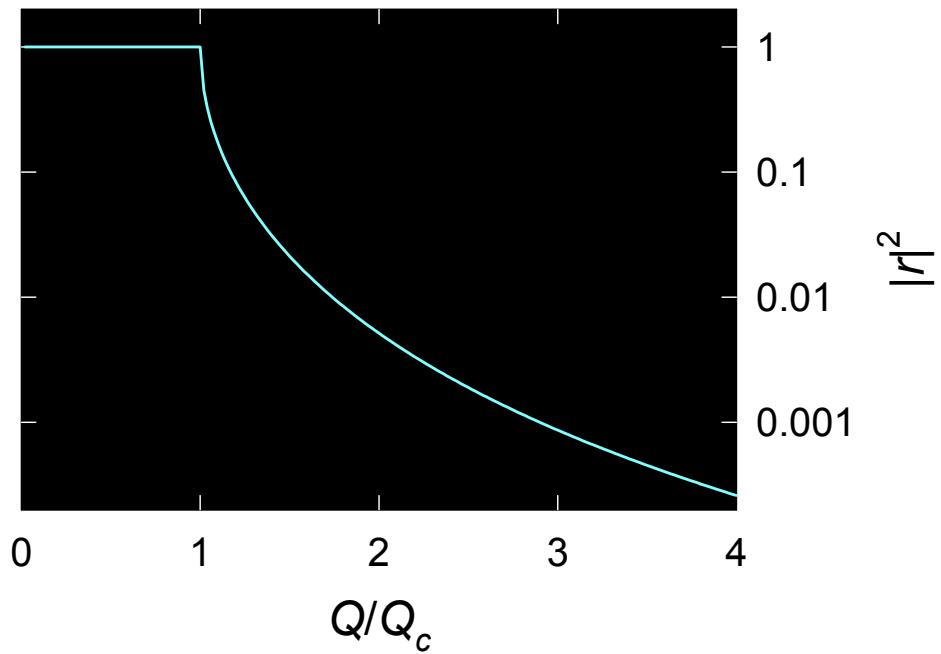
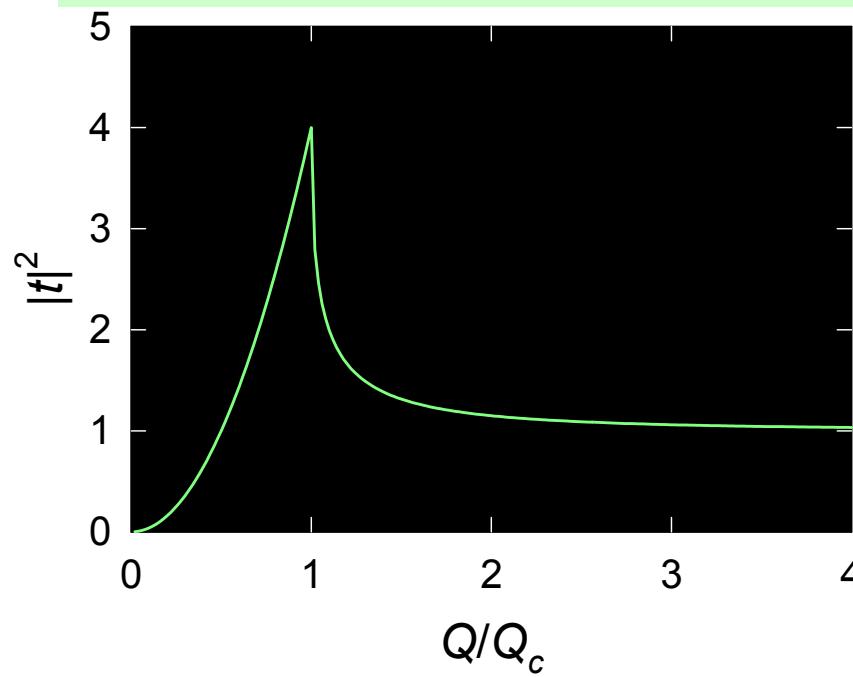
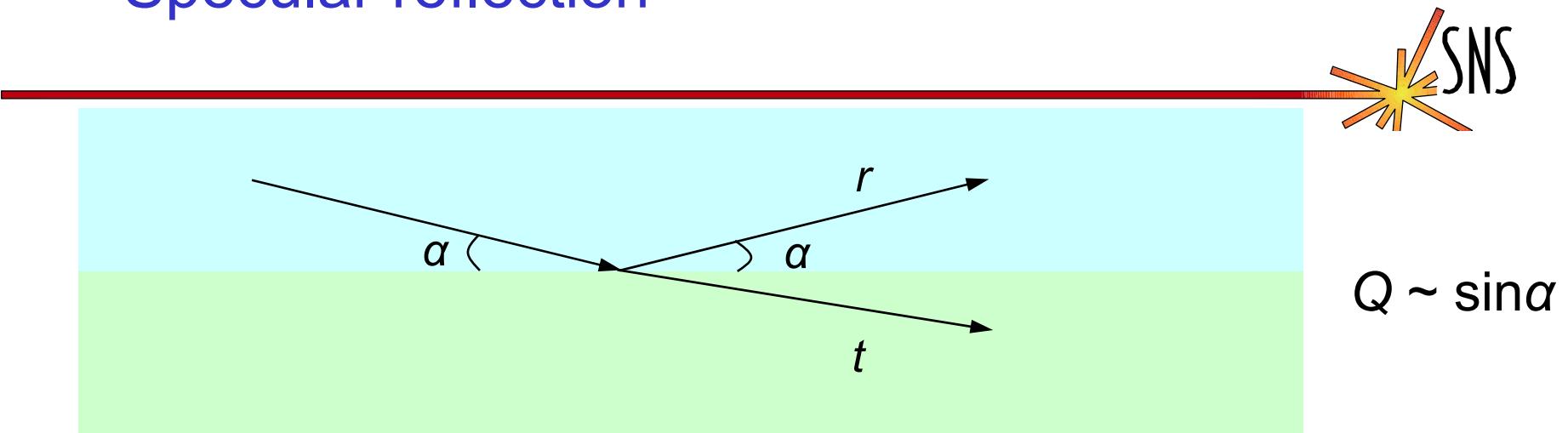
$$n_{\text{vacuum}} = 1$$

For yellow light in glass  
 $n \sim 1.5$

For thermal neutrons in glass  
 $n \sim 1 - (5 \times 10^{-6}) = 0.999995$



# Specular reflection



# Neutrons, x rays, and matter

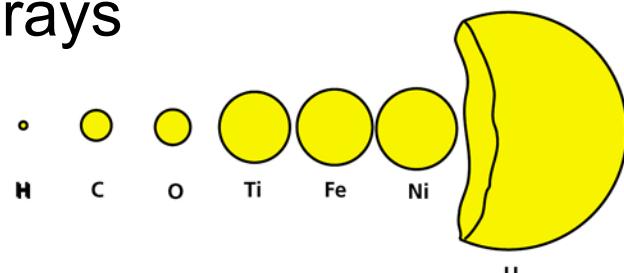


$$Q = 4\pi \sin\alpha / \lambda$$

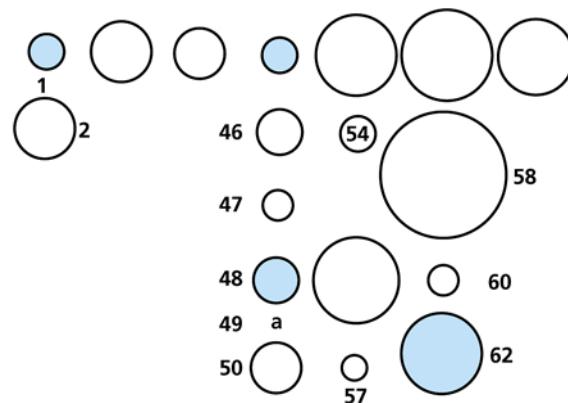
$$n \approx 1 - (bN)\lambda^2/2\pi$$

$$Q_c = 16\pi bN$$

X rays

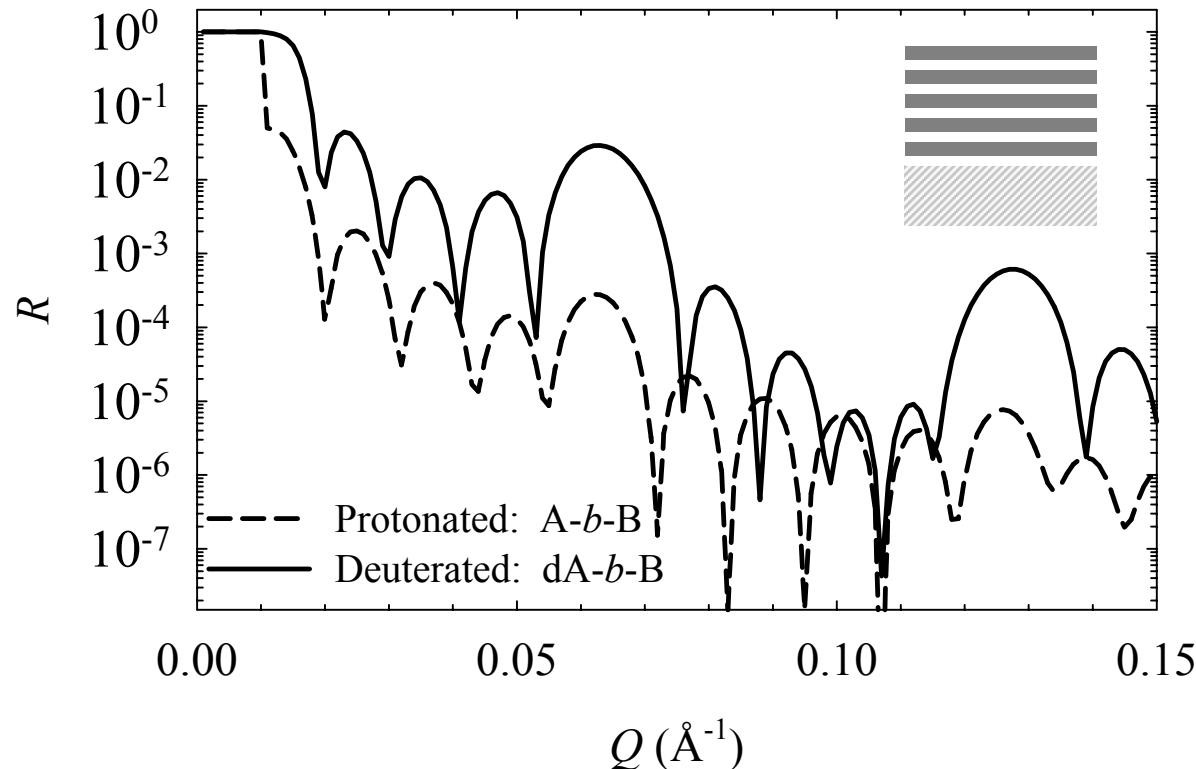


Neutrons



H C O Ti Fe Ni U

# Layers and multilayers; protium and deuterium

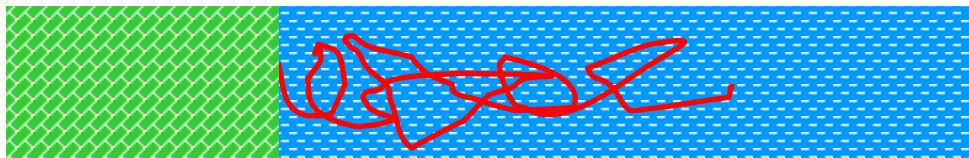


Reciprocal space  
 $Q \sim 2\pi/d$

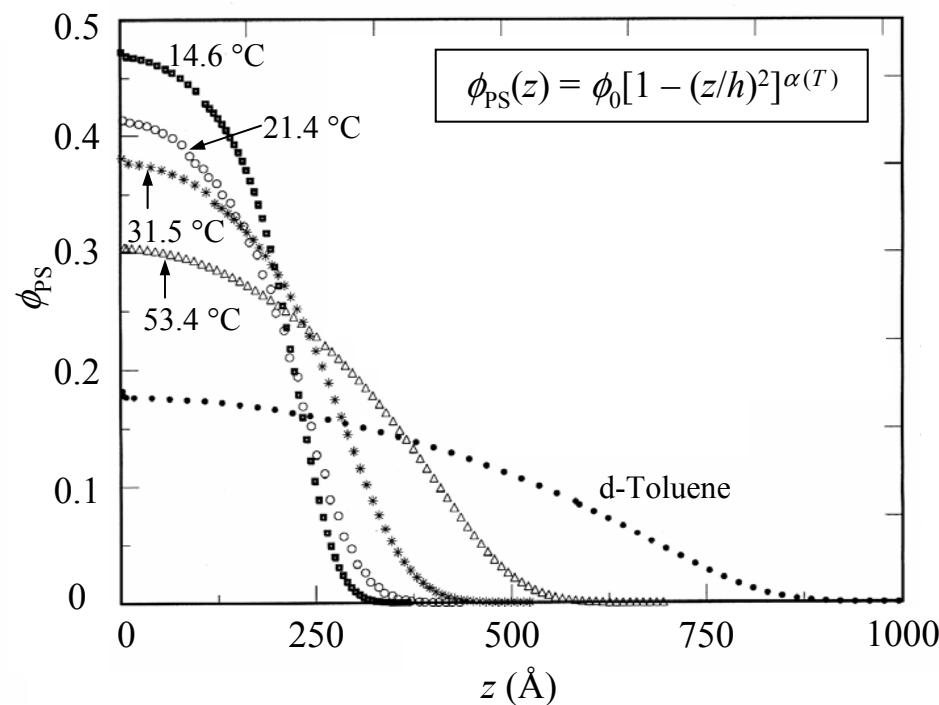
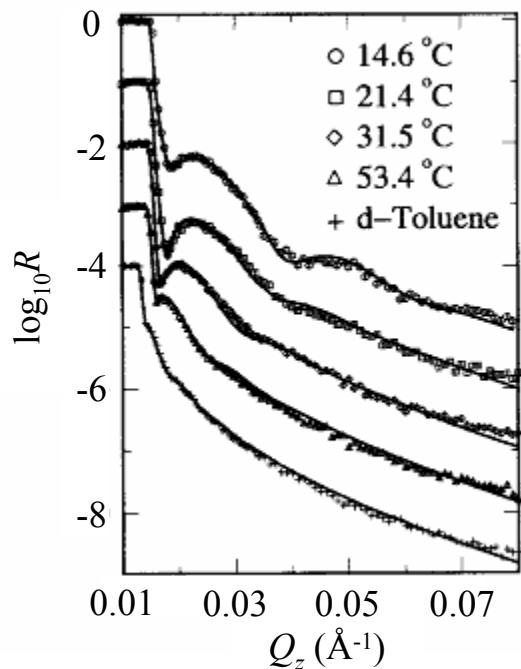
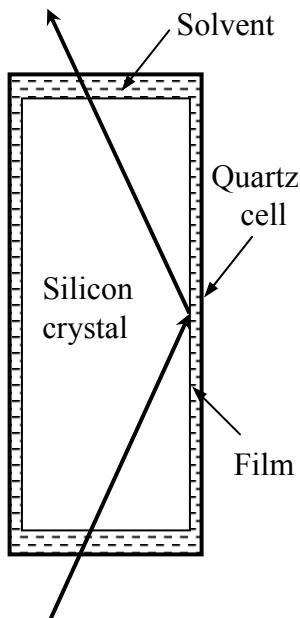
## Example: polymer brushes



Si



d-cyclohexane

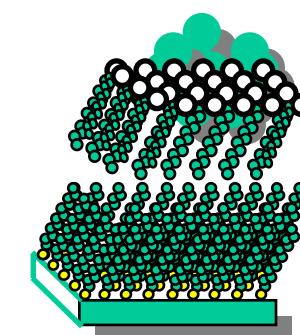
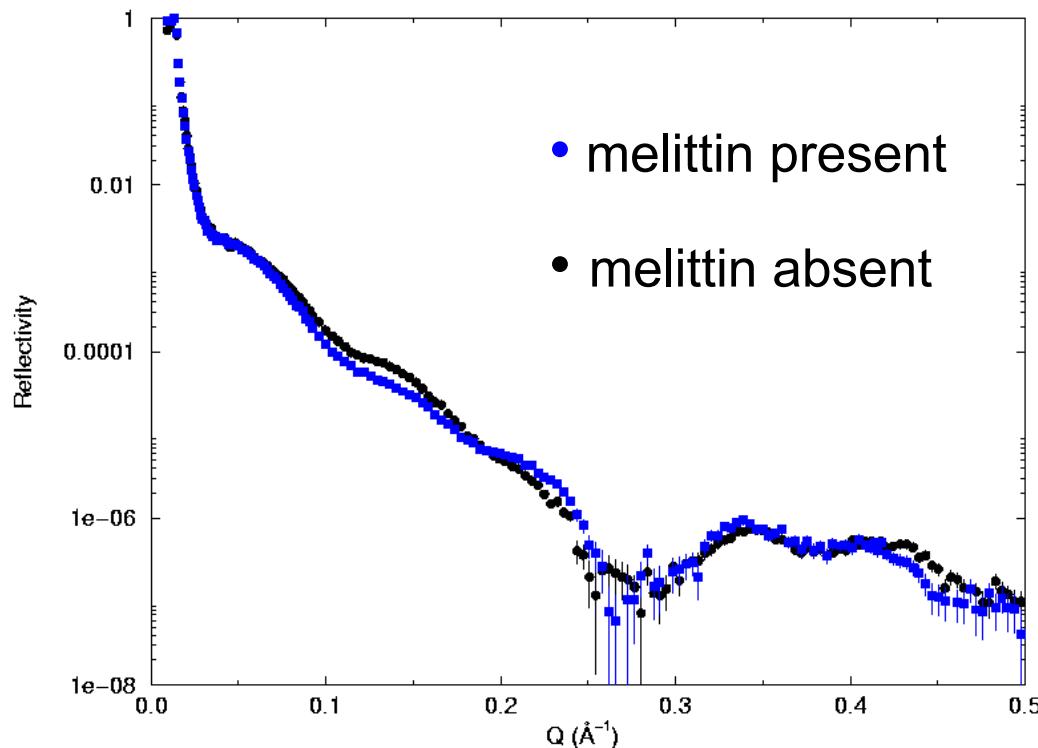


[A. Karim, et al., Phys. Rev. Lett. 73, 3407 (1994)]

# Example: protein interaction with membrane

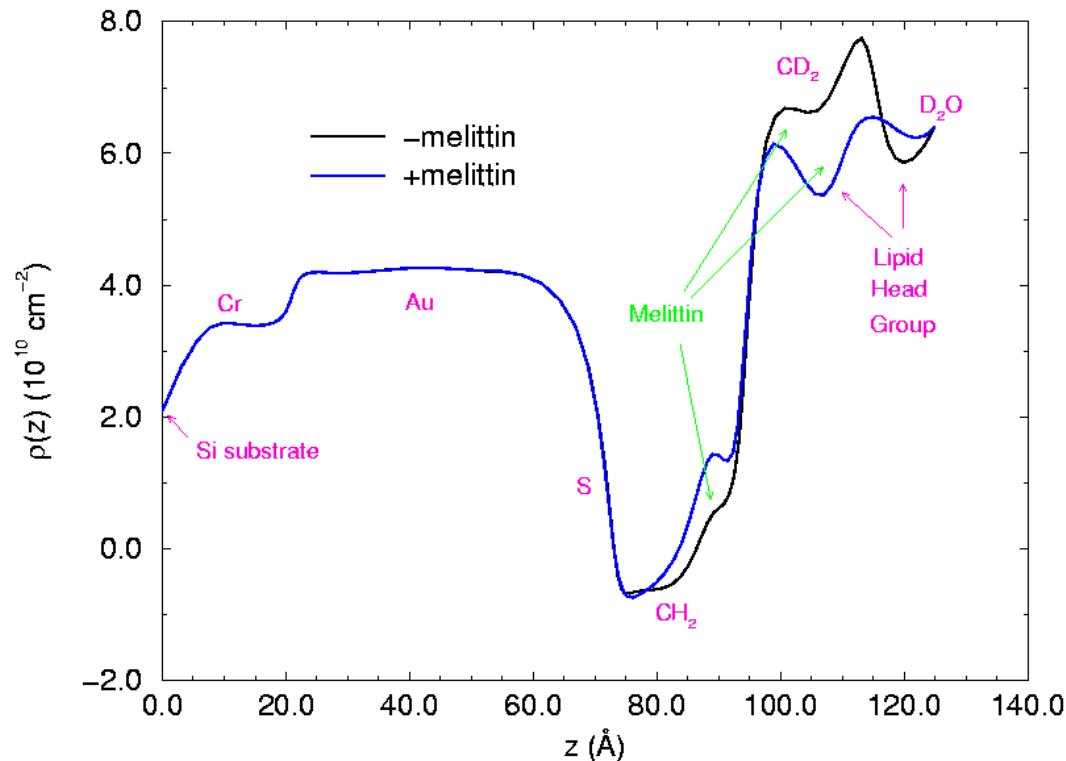


Melittin in alkanethiol/phospholipid hybrid bilayer membranes



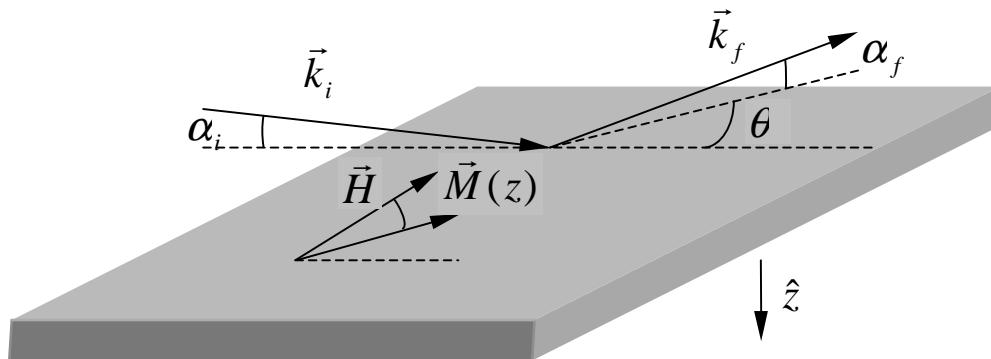
[Krueger, Meuse,  
Majkrzak, Dura, Berk,  
Tarek, and Plant,  
Langmuir 17, 511 (2001)]

# Phase-Sensitive Data Analysis



[Majkrzak, Berk, Krueger, Dura, Tarek,  
Tobias, Silin, Meuse, Woodward, and Plant,  
Biophys. J. 79, 3330 (2000)]

# What else reflectometers measure



## Specular

$$\begin{aligned}\alpha_i &= \alpha_f \\ \theta &= 0\end{aligned}$$

## Off-Specular

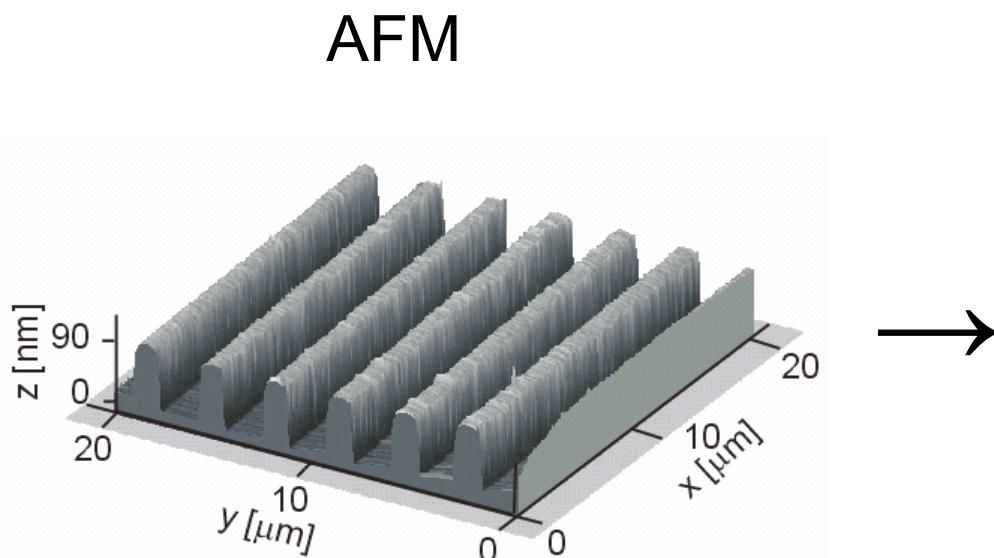
$$\begin{aligned}\alpha_i &\neq \alpha_f \\ \theta &= 0\end{aligned}$$

## GISANS

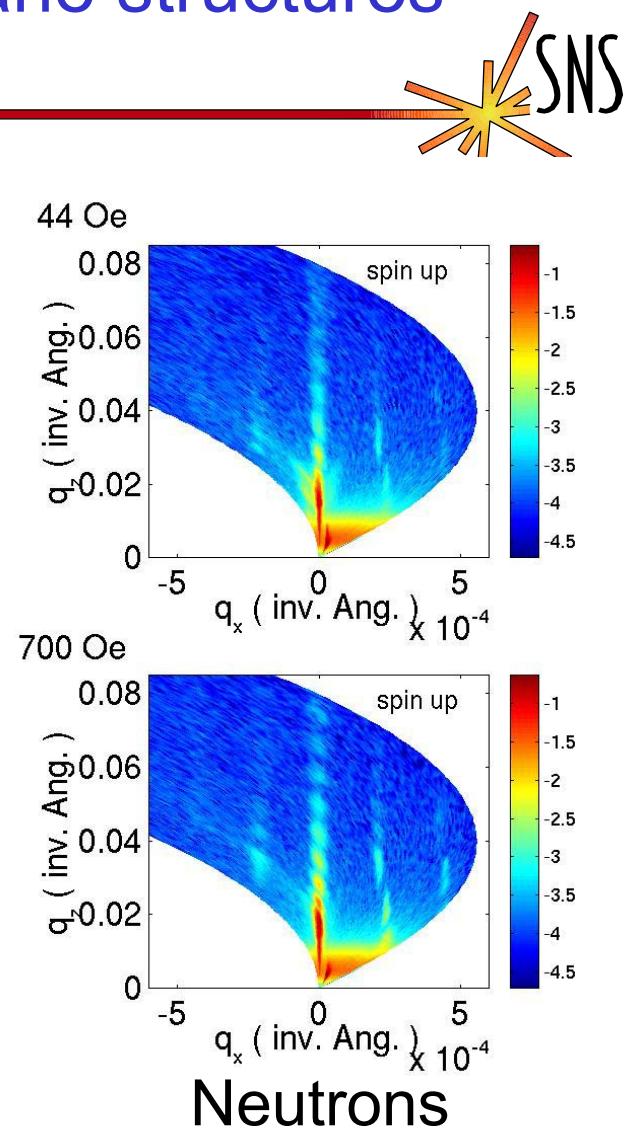
$$\begin{aligned}\alpha_i &\neq \alpha_f \\ \alpha_i, \alpha_f &< \sim \alpha_c \\ \theta &\neq 0\end{aligned}$$

Specular:  $Q = 4\pi \sin \alpha / \lambda$

# Off-specular data probes in-plane structures



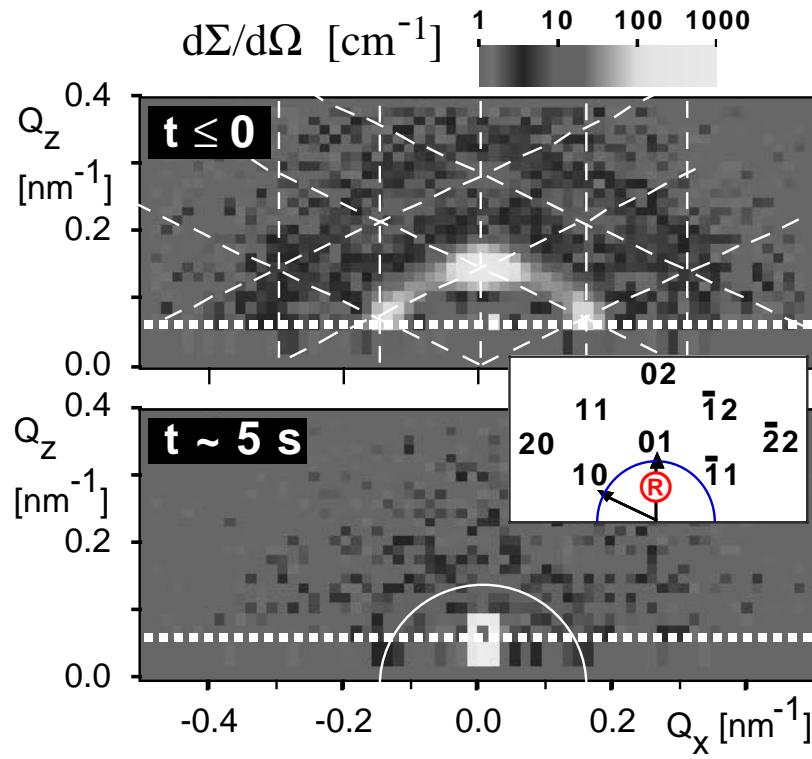
[K. Theis-Bröhl, et al., Phys. Rev. B, in press]



# Example: surface ordering of liquid crystal

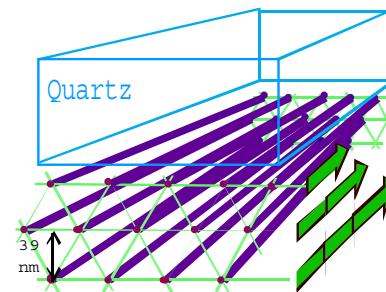


Relaxation of a shear induced crystalline surface phase  
ORNL/NIST



Under flow flexible surfactant micelles form hexagonal array near interface

W.A. Hamilton et al., *Physical Review Letters* **72**, 2219 (1994).



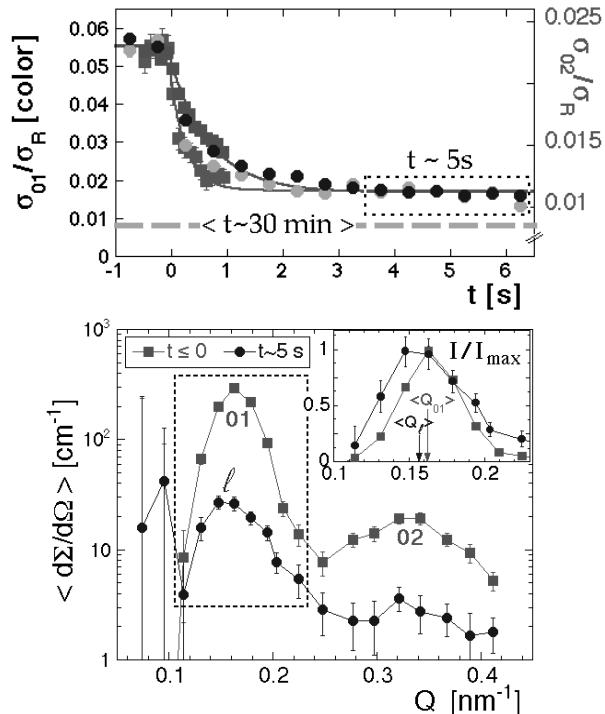
After flow is stopped:  
rapid decay "arc" of  
scattering

?

# Example: time-dependent measurements



Nature of the decay from "time-sliced" near-surface SANS



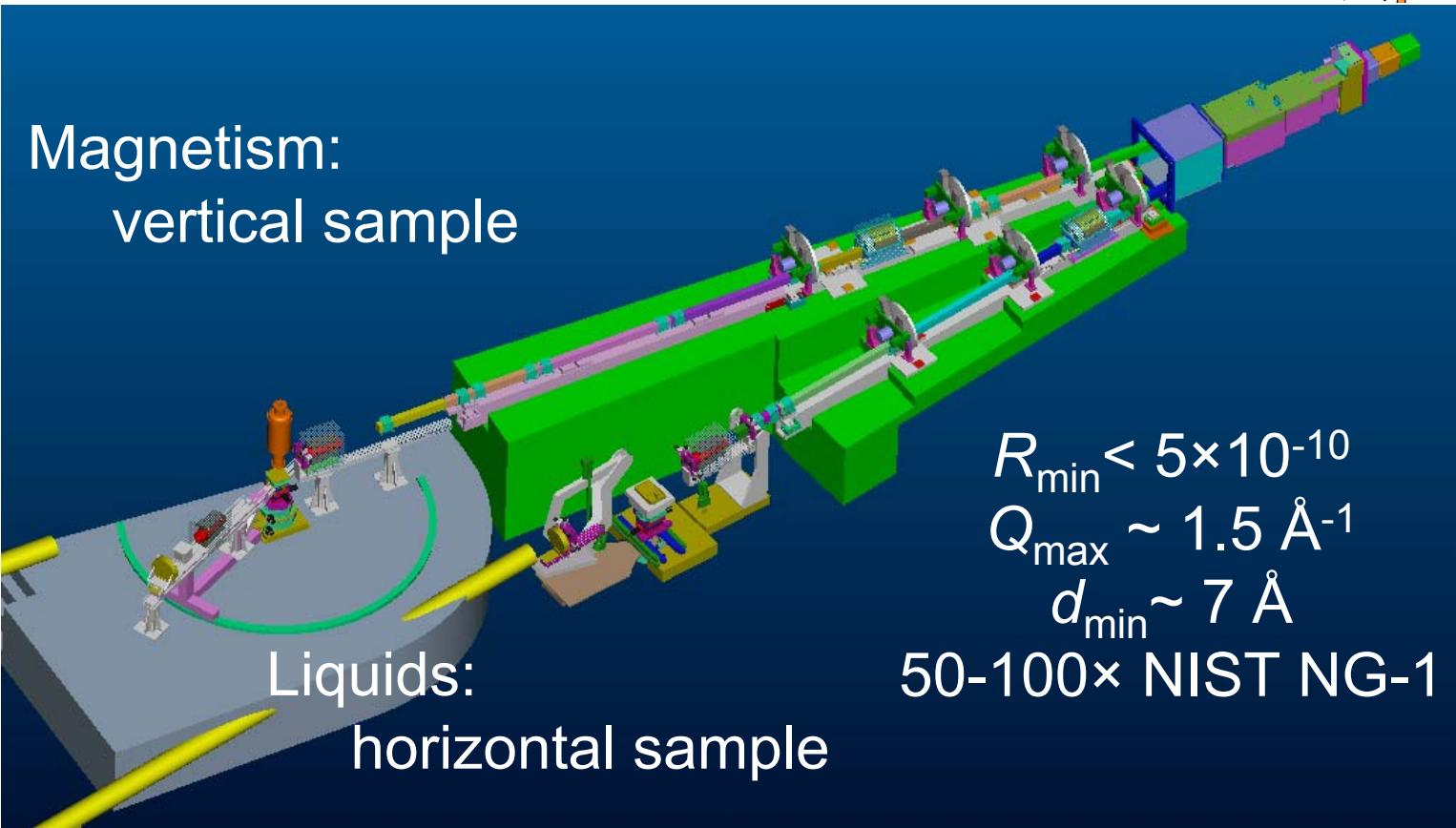
- Initial decay is rapid. First order peaks give way to arc in 0.7 s. Metastable intermediate state at  $t \sim 5$  s: full relaxation (bulk entanglement) takes ~30 minutes.
- As expected from Debye-Waller factor ( $\exp[-Q<\Delta r^2(t)>/2]$ ) second order peaks decay 4 times faster 0.1-0.2 s (gray).
- Small -3.3% shift between first order diffraction spot  $Q$  and that of the arc. This is consistent with the hexagonal phase rather than simple loss of crystalline alignment (arc is liquid peak rather than powder average).
- Metastable state is a liquid of aligned micelles.

W.A. Hamilton, P.D. Butler, L.J. Magid, Z. Han & T.M. Slawecki  
*Physical Review E (Rapid Communications)* **60**, R1146 (1999).

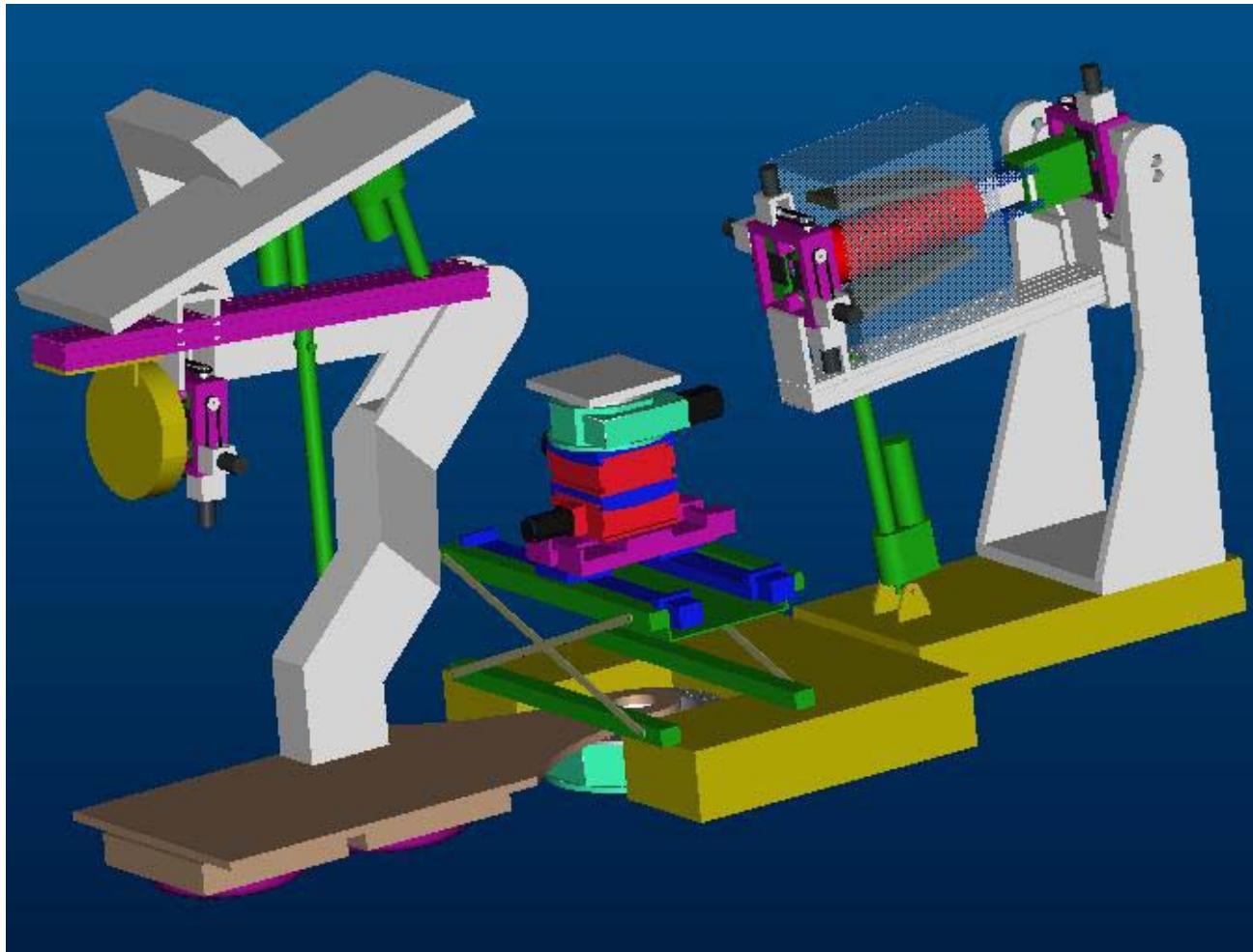


### III. What the Future Holds

# SNS shared reflectometer beamline



# Current instrument concept



## Design features



- Two reflectometers on beamline 4: one vertical and one horizontal sample surface
- Independent operation
- Multi-channel beam benders filter fast neutrons
- Tapered guides enhance flux-on-sample
- Each reflectometer uses three bandwidth choppers to allow operation from 6-60 Hz
- Sample tables designed to accommodate all types of reflectivity measurement and some diffraction
- Single  $^3\text{He}$  and 2D position-sensitive detectors

# A partial view of the future



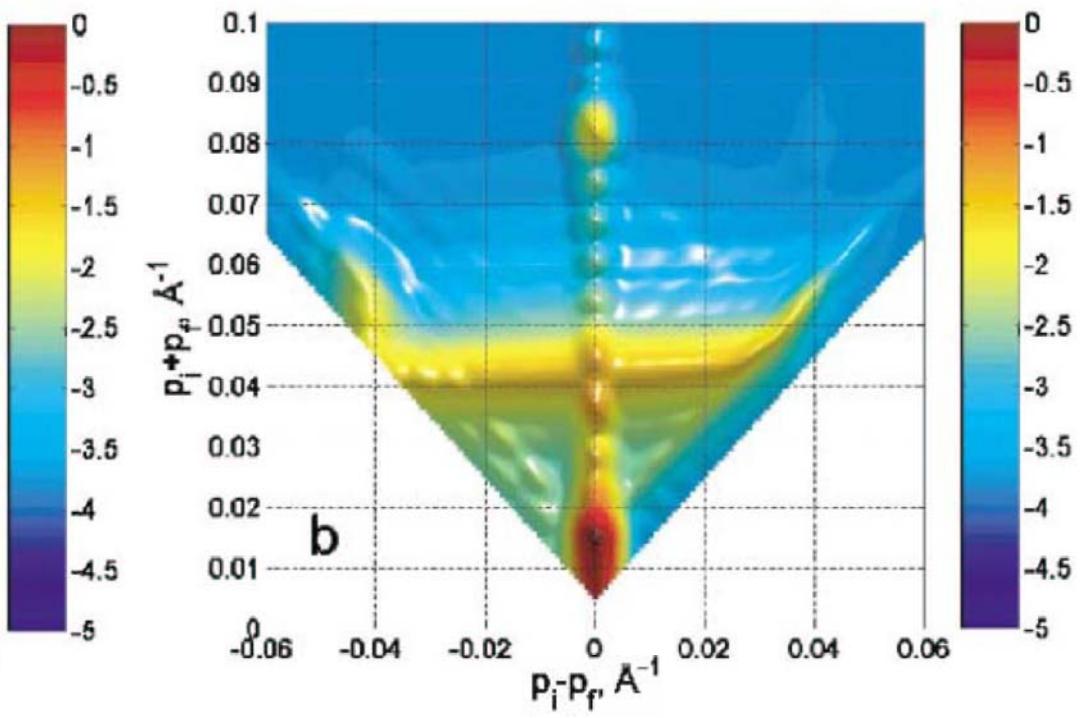
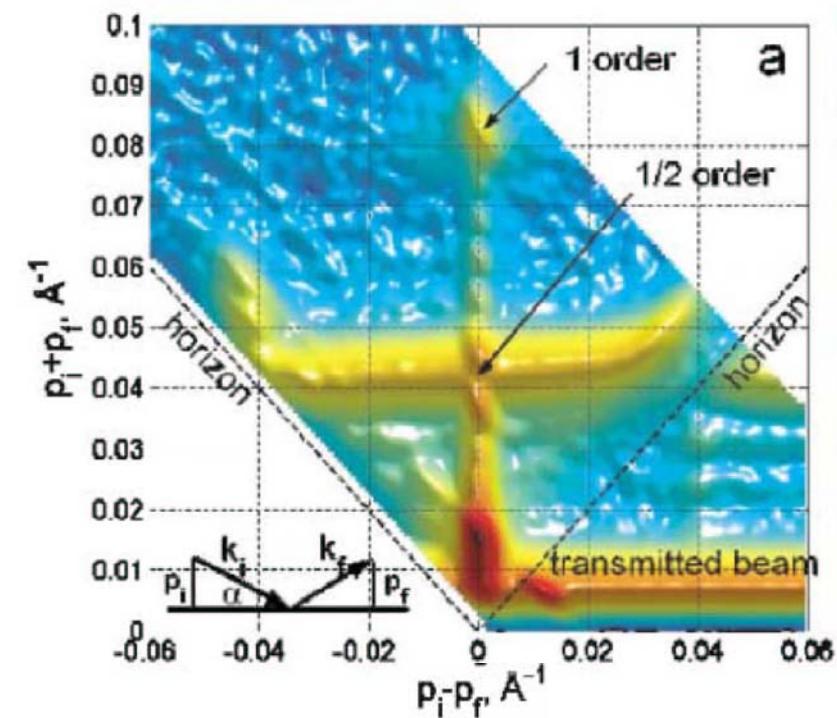
- Phase separation in polymer films
- Inorganic templating at air/water interfaces
- Complex fluids under flow
- Vesicles and gels
- Reaction kinetics
- Surfactants at interfaces
- Interfacial structure in drug delivery systems
- Membranes and their intermolecular interaction
- Protein adsorption
- Critical phenomena in fluid systems
- Biocompatibility and sensors

## New directions



- Routine parameter-free specular data analysis
- Routine off-specular measurements
- Time-dependent studies
- Pump-probe measurements
- Small samples
- Combinatorial measurements

## Example: routine off-specular measurements



[V. Lauter-Pasyuk, et al., Phys. Rev. Lett. 89, 167203 (2002)]